

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 10/00, 4/642	A1	(11) International Publication Number: WO 98/54230 (43) International Publication Date: 3 December 1998 (03.12.98)
(21) International Application Number: PCT/EP98/03099 (22) International Filing Date: 26 May 1998 (26.05.98) (30) Priority Data: 97108467.8 26 May 1997 (26.05.97) EP (34) Countries for which the regional or international application was filed: BE et al. (71) Applicant (for all designated States except US): FINA RESEARCH S.A. [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE). (72) Inventors; and (75) Inventors/Applicants (for US only): RAZAVI, Abbas [IR/BE]; Domaine de la Brisée 35, B-7000 Mons (BE). BELLIA, Vincenzo [IT/BE]; Rue Charles Bernier 4, B-7110 Mauraige (BE). (74) Common Representative: FINA RESEARCH S.A.; Patent Dept., Zone Industrielle C, B-7181 Seneffe (BE).		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METALLOCENE CATALYST COMPONENT FOR USE IN PRODUCING ISOTACTIC POLYOLEFINS		
(57) Abstract Provided is a metallocene catalyst component for use in preparing isotactic polyolefins, which component has the general formula (I): $R''(C_pR_1R_2R_3)(C_p'R'_n)MQ_2$ wherein C_p is a substituted cyclopentadienyl ring; C_p' is a substituted or unsubstituted fluorenyl ring; R'' is a structural bridge imparting stereorigidity to the component; R_1 is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR^*_3 in which X is chosen from Group IVA, and each R^* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R_2 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned <i>non-vicinal</i> to the distal substituent, and is of the formula $YR\#_3$, in which Y is chosen from Group IVA, and each $R\#$ is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, R_3 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and is a hydrogen atom or is of the formula $ZR\$_3$, in which Z is chosen from Group IVA, and each $R\$$ is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \leq n \leq 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

**METALLOCENE CATALYST COMPONENT FOR USE IN PRODUCING ISOTACTIC
POLYOLEFINS**

The present invention relates to a metallocene catalyst component for use in preparing isotactic polyolefins, especially polypropylenes. The invention further relates to a catalyst system which incorporates the metallocene catalyst component and a process for preparing such isotactic polyolefins.

Olefins having 3 or more carbon atoms can be polymerised to produce a polymer with an isotactic stereochemical configuration. For example, in the polymerisation of propylene to form polypropylene, the isotactic structure is typically described as having methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer. This can be described using the Fischer projection formula as follows:

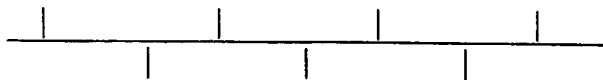


Another way of describing the structure is through the use of NMR spectroscopy. Bovey's NMR nomenclature for an isotactic pentad is ... mmmm with each "m" representing a "meso" diad or successive methyl groups on the same side in the plane.

In contrast to the isotactic structure, syndiotactic polymers are those in which the methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer. Using the Fischer projection formula, the structure of a syndiotactic polymer is described as follows:

CONFIRMATION COPY

- 2 -



In NMR nomenclature, a syndiotactic pentad is described as ...rrrr... in which "r" represents a "racemic" diad with successive methyl groups on alternate sides of the plane.

In contrast to isotactic and syndiotactic polymers, an atactic polymer exhibits no regular order of repeating unit. Unlike syndiotactic or isotactic polymers, an atactic polymer is not crystalline and forms essentially a waxy product.

While it is possible for a catalyst to produce all three types of polymer, it is desirable for a catalyst to produce predominantly an isotactic or syndiotactic polymer with very little atactic polymer. C_2 -symmetric metallocene catalysts are known in the production of the polyolefins. For example, C_2 symmetric *bis* indenyl type zirconocenes which can produce high molecular weight high melting isotactic polypropylene. The preparation of this metallocene catalyst is costly and time-consuming, however. Most importantly, the final catalyst consists of a mixture of racemic and meso isomers in an often unfavourable ratio. The meso stereoisomer has to be separated to avoid the formation of atactic polypropylene during the polymerisation reaction.

EP-A-0537130 discloses the use of a C_1 symmetric metallocene catalysts for the production of isotactic polypropylene. A preferred catalyst is isopropylidene (3-*t*-butyl-cyclopentadienyl fluorenyl)ZrCl₂. This catalyst has a bulky *t*-butyl group positioned on the cyclopentadienyl ring distal to the isopropylidene bridge. This catalyst has the advantage that it consists of only one stereoisomer and so no isomeric metallocene separation is required at the final stage of its synthesis. Whilst polypropylene preparation using this catalyst produces isotactic polypropylene, the polymer product has poor mechanical properties because of the presence of regiodefects and relatively

- 3 -

low molecular weight.

Regiodefects occur in the polymer chain when, instead of producing a perfect isotactic polyolefin in which each monomeric unit is positioned head-to-tail in relation to the next, mis-insertions of the monomers occur so as to give either a head-to-head or tail-to-tail mis-match. In the polymerisation process according to EP-A-0619325, there is a typical mis-insertion frequency of around 0.4%. These so called (2-1) regiodefects are partially transferred to the so called (1-3) insertion through an isomerisation process leaving units of four CH₂ groups in the backbone of the polypropylene chain. This has a deleterious effect on the physical and mechanical properties of the polymer and results in low molecular weight isotactic polypropylene with a low melting point.

The present invention aims to overcome the disadvantages of the prior art.

In a first aspect, the present invention provides a metallocene catalyst component for use in preparing isotactic polyolefins, which component has the general formula:



wherein C_p is a substituted cyclopentadienyl ring; C'_p is a substituted or unsubstituted fluorenyl ring; R'' is a structural bridge imparting stereorigidity to the component; R₁ is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR*₃, in which X is chosen from Group IVA, and each R* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R₂ is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned non-vicinal to the distal substituent, and is of the formula YR#₃, in which Y is chosen from group IVA, and each R# is the same or different and chosen from hydrogen or hydrocarbyl of

- 4 -

1 to 7 carbon atoms, R_3 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and is a hydrogen atom or is of the formula $ZR\$_3$, in which Z is chosen from group IVA, and each $R\$_$ is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \leq n \leq 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.

In one embodiment, the metallocene catalyst component of the present invention has the general formula:



wherein C_p is a substituted cyclopentadienyl ring; C_p' is a substituted or unsubstituted fluorenyl ring; R'' is a structural bridge imparting stereorigidity to the component; R_1 is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR^* , in which X is chosen from Group IVA, and each R^* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R_2 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned *non-vicinal* to the distal substituent and is of the formula $YR\#$, in which Y is chosen from group IVA, and each $R\#$ is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \leq n \leq 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.

Polyolefins produced using the metallocene catalyst component of the present invention are not only found to be isotactic but are also found to be substantially free of regiodefects. Accordingly, the polyolefins produced thereby have improved mechanical properties including a high weight average molecular weight typically of the order of 150,000-600,000 and elevated

- 5 -

melting point. Without wishing to be bound by any theory, it is postulated that the bulky group on the cyclopentadienyl ring contributes to the stereospecificity of the polymerisation reaction whereas the proximal substituent(s) on the cyclopentadienyl ring contribute to the regiospecificity of monomer insertion and the increase of molecular weight.

In the bulky distal substituent group R_1 , X is preferably C or Si. R^* may be a hydrocarbyl such as alkyl, aryl, alkenyl, alkylaryl or aryl alkyl, preferably methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl or phenyl. R_1 may comprise a hydrocarbyl which is attached to a single carbon atom in the cyclopentadienyl ring or may be bonded to two carbon atoms in that ring. Preferably, R_1 is $C(CH_3)_3$, $C(CH_3)_2Ph$, CPh_3 or $Si(CH_3)_3$, most preferably $C(CH_3)_3$.

The proximal substituents R_2 and R_3 are preferably CH_3 .

The structural bridge R'' is preferably alkylidene having 1 to 20 aliphatic or aromatic carbon atoms, a dialkyl germanium or silicon or siloxane, alkyl phosphene or amine bridging the two C_p rings. R'' is preferably dimethylsilanediyl in which the two C_p rings are bridged by the silicon atom, or isopropylidene in which the two C_p rings are bridged by position 2 of the isopropylidene.

M is preferably zirconium or titanium, most preferably zirconium. Q may be a hydrocarbyl such as alkyl, aryl, alkenyl, alkylaryl or aryl alkyl, preferably methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl or phenyl. Q is preferably a halogen.

The fluorenyl ring C_p' can have up to 8 substituent groups R'_n , each of which is the same or different and may be a hydrocarbyl selected from alkyl, aryl, alkenyl, alkyl aryl or aryl alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl,

- 6 -

isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl or phenyl. These substituents must be selected so that they do not interfere with coordination of the monomer to the metal. Preferably, therefore, the fluorenyl ring is unsubstituted at both positions 4 and 5, these positions being distal to the bridge.

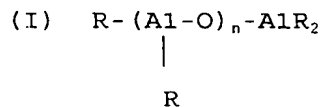
In a further aspect, the present invention provides a metallocene catalyst component for use in preparing isotactic polyolefins, which comprises (i) a catalyst component as defined above; and (ii) a regioisomer thereof in which R_2 is proximal to the bridge and positioned vicinal to the distal substituent.

Such regioisomers are frequently relatively easy to prepare because they are formed as a "by-product" during the synthetic route by which the catalyst component (i) may be made.

Surprisingly, it has been found that catalyst components including both regioisomers can be used in the preparation of isotactic polyolefins which have a multimodal, especially a bimodal, molecular weight distribution.

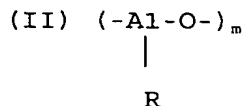
In a further aspect, the present invention provides a catalyst system for use in preparing isotactic polyolefins, which comprises (a) a catalyst component as defined above; and (b) an aluminium- or boron-containing co-catalyst capable of activating the catalyst component. Suitable aluminium-containing co-catalysts comprise an alumoxane, an alkyl aluminium and/or a Lewis acid.

The alumoxanes usable in the process of the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula:



- 7 -

for oligomeric, linear alumoxanes and



for oligomeric, cyclic alumoxane, wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈ alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

Suitable boron-containing co-catalysts may comprise a triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696, or those of the general formula [L'-H] + [B Ar₁ Ar₂ X₃ X₄]- as described in EP-A-0277004 (page 6, line 30 to page 7, line 7).

The catalyst system may be employed in a solution polymerisation process, which is homogeneous, or a slurry process, which is heterogeneous. In a solution process, typical solvents include hydrocarbons with 4 to 7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided

- 8 -

functionalised polyolefins such as finely divided polyethylene.

Preferably, the support is a silica having a surface area comprised between 200 and 700 m²/g and a pore volume comprised between 0.5 and 3 ml/g.

The amount of alumoxane and metallocenes usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably the aluminium to transition metal mole ratio is in the range between 1:1 and 100:1, preferably in the range 5:1 and 50:1.

The order of addition of the metallocenes and alumoxane to the support material can vary. In accordance with a preferred embodiment of the present invention alumoxane dissolved in a suitable inert hydrocarbon solvent is added to the support material slurried in the same or other suitable hydrocarbon liquid and thereafter a mixture of the metallocene catalyst component is added to the slurry.

Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperature and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene.

Preferably the support material is slurried in toluene and the metallocene and alumoxane are dissolved in toluene prior to addition to the support material.

In a further aspect, the present invention provides use of a catalyst component as defined above and a co-catalyst which activates the catalyst component, for the preparation of isotactic polyolefins, preferably polypropylenes. In a still further aspect, the present invention provides use of a

- 9 -

metallocene catalyst component comprising (i) the catalytic component and (ii) a regioisomer thereof, in which R_2 is proximal to the bridge and positioned vicinal to the distal substituent, for the preparation of isotactic polyolefins, especially polypropylenes, having a multimodal molecular weight distribution, preferably a bimodal molecular weight distribution.

In a further aspect, the present invention provides a process for preparing isotactic polyolefins, especially polypropylenes, which comprises contacting a catalyst system as defined above with at least one olefin, preferably propylene, in a reaction zone under polymerisation conditions.

The catalyst component may be prepared by any suitable method known in the art. Generally, the preparation of the catalyst component comprises forming and isolating bridged dicyclopentadiene, which is then reacted with a halogenated metal to form the bridged metallocene catalyst.

In one embodiment, the process for preparing the bridged metallocene catalyst components comprises contacting a substituted cyclopentadiene having bulky and non bulky substituents on the cyclopentadienyl ring with a fluorene under reaction conditions sufficient to produce a bridged substituted dicyclopentadiene. The process further comprises contacting the bridged substituted dicyclopentadiene with a metal compound of the formula MQ_k as defined above under reaction conditions sufficient to complex the bridged dicyclopentadiene to produce a bridged metallocene wherein M and Q are each defined as above and $0 \leq k \leq 4$. The process step of contacting the bridged substituted dicyclopentadiene with a metal compound can be performed in a chlorinated solvent.

In a further embodiment, the process comprises contacting a substituted cyclopentadiene having bulky and non bulky substituents on the cyclopentadienyl ring with an alkyl silyl chloride of the formula $R^{\sim}_2SiHal_2$, wherein R^{\sim} is a hydrocarbyl

- 10 -

having 1 to 20 carbon atoms and Hal is a halogen. A second equivalent of an optionally substituted fluorene is added to produce a silicon bridged substituted cyclopentadienyl-fluorenyl ligand. The subsequent steps are similar to those above for producing a bridged disubstituted cyclopentadienyl-fluorenyl ligand coordinated to metals such as Zr, Hf and Ti.

In a further embodiment, the process comprises contacting a substituted cyclopentadiene with a fulvene producing agent such as acetone to produce a substituted fulvene. Subsequently, in a second step, the fulvene is reacted with fluorene to produce a carbon bridged substituted cyclopentadienyl-fluorenyl ligand that will produce the desired metallocene catalysts after reacting with MCl_4 , in which M is Zr, Hf or Ti.

The invention will now be described in further detail, by way of example only, with reference to the attached drawings in which:

FIGURE 1 shows an illustration of the three-dimensional structure of a preferred catalyst component of the present invention as obtained by X-ray diffraction analysis of isopropylidene (3-tert. butyl-5-methyl cyclopentadienyl-fluorenyl) Zr Cl_2 ;

FIGURE 2 shows an illustration of the three-dimensional structure of a preferred catalyst component of the present invention as obtained by X-ray diffraction analysis of isopropylidene (3-tert. butyl-2-methyl cyclopentadienyl-fluorenyl) Zr Cl_2 ;

FIGURE 3 shows the results of gel permeation chromatography on isotactic polypropylene produced at 40°C using a mixture of the isomers shown in Figures 1 and 2 as a catalyst component; and

FIGURE 4 shows the results of gel permeation chromatography on isotactic polypropylene produced at 60°C using a mixture of the isomers shown in Figures 1 and 2 as a catalyst component.

- 11 -

Example 1: Synthesis of isopropylidene(3-t-butyl-5-methylcyclopentadienyl fluorenyl)ZrCl₂.

A) Synthesis of the trimethyl fulvene.

In a round bottom flask equipped with magnetic stirring bar and nitrogen inlet is placed 350 ml of methanol (at -78°C) containing freshly prepared methylcyclopentadiene under nitrogen. To this solution is added a solution of 28.6 g of acetone in 50 ml of methanol drop wise. Subsequently 52.5 g of pyrrolidine is added. The reaction mixture is stirred at ambient temperature for 24 hours. After neutralization with acetic acid and separation of the organic phase the solvent is evaporated and the remaining yellow oil is subjected to distillation. A mixture of 6,6,3-trimethyl fulvene and 6,6,5,-trimethyl fulvene is obtained in 65% yield.

B) Synthesis of methyl-t-butyl-cyclopentadiene.

The product obtained in step A is placed in 2l flask and dissolved in 350 ml of diethyl ether and cooled down to 0°C. To the solution is added drop wise 140.6 ml of methyl lithium in ether (1.6 mol). The reaction is completed after a few hours. After adding 40 ml of saturated solution of NH₄Cl in water the organic phase is separated and dried with MgSO₄. The evaporation of the solvent leads to the isolation of a yellow oil as two stereo isomers quantitatively.

C) Synthesis of t-butyl-trimethyl-fulvene.

In a 500 ml flask is placed 12.60 g of the product obtained in step B and dissolved in 40 ml of methanol. The mixture is cooled down to -78°C. 2.15 g acetone in 10 ml of ethanol is added slowly. In the next step 4 g of pyrrolidine in 10 ml of methanol is added. After six hours the reaction is terminated by addition of 10 ml of acetic acid. After separation of organic phase,

- 12 -

drying, evaporation of solvents and distillation an orange oil is obtained (8.95 g).

D) Synthesis of 2,2-[(3-t-butyl-methyl-cyclopentadienyl) fluorenyl]propane.

In round bottom flask is placed 3.8 g fluorene in 100 ml of THF under nitrogen. 14.2 ml of methyl lithium in ether (1.6 mol) is added. The reaction mixture is stirred for 3 hours and then reacted with 4.70 g of the product obtained in step C dissolved in 10 ml of THF. The reaction is terminated after 8 hours by the addition of a saturated solution of NH_4Cl in water. The organic phase is separated, the solvents evaporated and 8.5 g of the title compound is obtained as an oily mixture of two principal isomomers, 2,2-[(3-t-butyl-5-methyl-cyclopentadienyl) fluorenyl]propane and 2,2-[(3-t-butyl-2-methyl-cyclopentadienyl) fluorenyl]propane.

E) Synthesis of the mixture of isopropylidene(3-t-Bu-5-methyl-cyclopentadienyl fluorenyl) ZrCl_2 (1) and isopropylidene(3-t-Bu-2-methyl-cyclopentadienyl fluorenyl) ZrCl_2 (2).

2 g of the ligand obtained in step D is dissolved in 250 ml THF under nitrogen and reacted with 7.3 ml methyl lithium in ether (1.6 mol). The reaction mixture is stirred over night. The solvent is evaporated next day and the dianion of the ligand is isolated which is reacted with 3.8 g of ZrCl_4 in 200 ml ether at -78°C . The mixture is stirred for 6 hours at room temperature. The two isomers can be separated by solvent separation since (1) is less soluble in dichloromethane than (2).

Isopropylidene(3-t-butyl-5-methyl-cyclopentadienyl fluorenyl) ZrCl_2 is recovered, the structure of which is shown in Figure 1.

- 13 -

Example 2: Synthesis of isopropylidene (3-t-butyl-2-methyl-cyclopentadienyl fluorenyl)ZrCl₂

The synthetic procedure according to Example 1 is followed except that, after solvent separation at the end of step E, isopropylidene(3-t-butyl-2-methyl-cyclopentadienyl fluorenyl)ZrCl₂ is recovered. The structure of this isomer is shown in Figure 2.

Example 3: Synthesis of mixture of isopropylidene(3-t-butyl-5-methylcyclopentadienyl fluorenyl)ZrCl₂ and isopropylidene(3-t-butyl-2-methylcyclopentadienyl fluorenyl)ZrCl₂.

The synthetic procedure according to Example 1 is followed except that the step of solvent separation of the two isomers is omitted.

Example 4: Polymerisation procedures I

Each polymerisation was performed in a 4 litre bench reactor with pure propylene or with diluent such as cyclohexane or isobutane with the quantities reported in the following Tables. Polymerisation was initiated by introducing metallocene (0.5 to 5 mg) pre-contacted with 1 ml of MAO (methylaluminoxane) (30% solution in toluene obtained from WITCO) three minutes prior to its introduction into the reactor.

Tables 1 and 2 show the results of polypropylene production using the catalyst system of Example 1. Entries 1 to 4 compare polymerisation of pure propylene (bulk - entry 1) with those using the diluents cyclohexane (entry 2) and isobutane at two different partial pressures of hydrogen (entries 3 and 4). The polymerisation temperature for each of these entries was 60°C. Entries 5 and 6 compare bulk propylene polymerisation at the higher temperatures of 70°C and 80°C respectively. It is apparent that a molecular weight of about 200,000 to about

- 14 -

450,000 was obtainable. Polypropylene having a melt temperature of at least 139°C was obtained, in this case around 140°C. The polymers obtained exhibited monomodality on gel permeation chromatography (results not shown).

Table 1 - Polymerization with iPr(5-Me-3-tBu-Cp Flu)ZrCl₂

Entry	Pol.	Hourly prod.	MI ₂ (g/10min)	Mn (Da)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
1	60	54,000	3.64	67,700	458,500	1,334,000	6.8	2.9	142.4
2	60	50,500	1.74	120,000	402,200	936,000	3.4	2.3	143.8
3	60*	96,000	3.08	74,400	333,800	880,000	4.5	2.6	142.6
4	60**	110,000	13.56	68,000	248,600	581,000	3.7	2.3	142.2
5	70	110,500	7.53	74,200	306,000	1,066,000	4.1	3.5	139.3
6	80	130,000	13.50	62,800	213,900	499,000	3.4	2.3	139.6

Key: MI₂ = Melt index; Mn = number average molecular weight; Mw = weight average molecular weight;

D = Mw/Mn; D' = Mz/Mw

1. Bulk Propylene; 2. Slurry in Cyclohexane; 3. Slurry in isobutane

(*) : 0.25 NI H2; (**) : 1 NI H2

- 16 -

Table 2 shows the microtacticity of the polymer obtained using the catalyst according to Example 1 under polymerisation conditions as defined by the corresponding entries in Table 1. The results were obtained using ^{13}C NMR spectroscopy. It will be apparent that the polypropylene contained more than 80% of pentads in the purely isotactic form (mmmm) and a virtually undetectable frequency of misinsertions.

Tables 3 and 4 show corresponding data in relation to the bulk polymerisation of propylene using the catalyst system of Example 2. The weight average molecular weight of the polypropylene in this case is much lower than for the polypropylene produced using the catalyst of Example 1. The melt temperatures reported in Table 3 are also lower than those in Table 1. Table 4 shows the microtacticity of the polymers of the two entries in Table 1 from which it will be apparent that the percentage of purely isotactic pentads is reduced as compared with those reported in Table 2. Importantly, a misinsertion frequency of up to 0.4% is found in Table 4 as compared with the virtually undetectable frequency of misinsertions reported in Table 2.

Table 2
Microtacticity with $iPr(5-Me-3-tBu-Cp\ Flu)ZrCl_2$

Entry	mmmm%	mmmr%	mmrr%	mrrm%	inversion %	NMR Scans
1	85.8	5.3	5.1	2.5	not det.	2224
2	86.8	5.2	4.7	2.3	(1)	4080
3	83.9	6.1	5.3	2.5	(1)	4344
4	84.0	5.8	5.2	2.5	(1)	2368
5	82.8	6.3	5.6	2.7	/	2272
6	83.8	6.2	5.4	2.4	(1)	7128

(1): inversions observed but too low to be quantified.

Table 3 - Bulk polymerization with $iPr(2-Me-3-tBu-Cp)Flu)ZrCl_2$

Entry	Pol. Temp (°C)	Hourly prod. (gPP/gCat/h)	Mn (Da)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
1	40	179,000	37,400	96,600	409,000	2.6	4.2	101.4
2	60	99,000	22,100	73,800	431,000	3.3	5.8	110.9

Key: MI_2 = Melt index; Mn = number average molecular weight; Mw = weight average molecular weight;
 $D = Mw/Mn$; $D' = Mz/Mw$

- 19 -

Table 4 - Microtacticity with iPr(2-Me-3-tBu-Cp Flu)ZrCl₂

Entry	Pol.Temp. (°C)	mmmm%	mmmr%	mmrr%	mrmm%	Inv. %	NMR Scans
1	40	61.1	12.3	13.4	6.0	0.2-0.4	5000
2	60	69.3	10.6	10.3	4.9	0.1-0.2	3976

Table 5

Bulk polymerization with the mixture of isomers

iPr(2-Me-3-tBu-Cp Flu)ZrCl₂ + iPr(5-Me-3-tBu-Cp Flu)ZrCl₂

Entry	Pol.	Hourly prod.	Mn (gPP/gCat/h)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
1	40	2,250	27,800	336,700	1,524,000	12.1	4.5	133.1
2	60	5,200	45,700	255,000	906,800	5.6	3.6	136.7

Key: M_L = Melt index; M_n = number average molecular weight; M_w = weight average molecular weight;D = M_w/M_n; D' = M_z/M_w

- 21 -

Tables 5 and 6 show the results of corresponding bulk propylene polymerisation with a mixture of the two isomers from Examples 1 and 2. These polymers have relatively high melt temperatures. However, unlike the polymers reported in Table 1 using the single isomer isopropylidene (3-t-butyl-5-methylcyclopentadienyl fluorenyl)ZrCl₂, which exhibits monomodality on gel permeation chromatography, polymers produced using the mixture of isomers exhibit bimodality. This is apparent from Figures 3 and 4 which show respectively the results of gel permeation chromatography on the polymers of entries 1 and 2 of Table 5.

Table 6 shows steric pentad concentrations and regiodefects concentrations.

-22-

Table 6
 iPr(2-Me-3-tBu-Cp Flu)ZrCl₂ + iPr(5-Me-3-tBu-Cp Flu)ZrCl₂

Entry	Pol.Temp (°C)	mmmm%	mmmr%	mmrr%	mmrr%	Inv. %
1	40	62.0	10.6	11.8	4.8	0.3
2	60	74.3	8.2	8.17	3.65	nd

- 23 -

Example 5: Synthesis of dimethylsilyl(2,5-dimethyl-3-t-butyl-cyclopentadienyl fluorenyl)zirconium dichlorideFormula: $\text{Me}_2\text{Si}(2,5\text{-Me}_2\text{-3-tBu-Cp flu})\text{ZrCl}_2$ $\text{C}_{26}\text{H}_{30}\text{SiZrCl}_2$

Mw: 532.68

A. Preparation of 1,3-dimethylcyclopentadiene

Reaction:

Ether, 0°C

3-Me-2-cyclopentenone + Me-MgBr ----->

1,3-Me₂-3-OMgBr-2-cyclopentene1,3-Me₂-3-OMgBr-2-cyclopentene + H₂O ----->1,3-Me₂-2-cyclopenten-3-ol

84-86°C

1,3-Me₂-2-cyclopenten-3-ol ----->1,3-Me₂-cyclopentadiene

Procedure:

In a flask under nitrogen, were placed 200 ml (0.6 mol.) of methylmagnesium bromide (3.0 molar in ether) and 200 ml of dry ether at 0°C. Then a solution of 49.19 g (0.5117 mol.) of 3-methyl-2-cyclopentenone in 50 ml of dry ether was added dropwise to this solution. After a stirring period (one hour), the reaction mixture was yellow-red. The reaction was further continued at room temperature for 24 hours. The reaction mixture was treated with 500 ml of water cooled to 0°C. After separation and drying over anhydrous MgSO₄, the solvent of the organic phase

- 24 -

was removed in vacuo (500 - 550 mbars) to room temperature. The viscous red oil was distilled and collected at -78°C. Fractional distillation at 84-86 °C yielded 24.10 g (50.14%) of a clear colorless liquid, containing a small quantity (ca. 5%) of 1-methylcyclopentadiene.

B. Preparation of 1,3,6,6-tetramethylfulvene

Reaction:

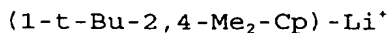
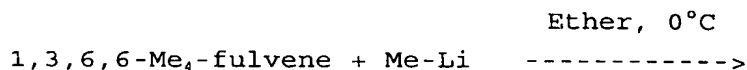


Procedure:

In a 250 ml flask, under nitrogen, were placed 50 ml of methanol at -78°C. Then 24.10g (0.256 mol.) of 1,3-dimethylcyclopentadiene was added to the methanol. After that, a solution of 7.5 ml (0.102 mol.) of acetone in 25 ml of methanol was added dropwise to this solution. Finally, a solution of 12.8 ml (0.154 mol.) of pyrrolidine in 25 ml of methanol was added dropwise to the reaction mixture. After an hour, the reaction mixture was red and the reaction was further continued for 2 days. After neutralization with 10 ml of acetic acid and 50 ml of water, the reaction mixture was separated and dried over anhydrous MgSO_4 . The solvent of the organic phase was removed in vacuo (10-2 mbar) and yielded 15.62 g (45.45%) of a clear red liquid.

C. Preparation of 1-t-butyl-2,4-dimethyl cyclopentadiene

Reaction:



- 25 -

(1-t-Bu-2,4-Me₂-Cp) -Li⁺ H₂O ----->

1-t-Bu-2,4-Me₂-cyclopentadiene

Procedure:

In a 1 liter flask, under nitrogen, were placed 200 ml of dry ether and 15.20 g (0.113 mol.) of 1,3,6,6-tetramethylfulvene. The yellow solution was cooled to 0°C. Then, a solution of 70.8 ml (0.113 mol.) of methyllithium (1.6 molar in ether) was added dropwise to this solution. The reaction was further continued at room temperature for 24 hours. The reaction mixture was treated with 50 ml of solution of NH₄Cl (saturated). After separation and drying over anhydrous MgSO₄, the solvent of the organic phase was removed in vacuo (10-2 mbar) and yielded 13.21 g (77.63%) of a clear yellow oil.

D. Preparation of chlorodimethyl-(9-fluorenyl)silane

Reaction:

Ether

fluorene + Me-Li -----> fluorenyllithium
0°C

Hexane

fluorenyllithium + Me₂SiCl₂ ----->

chlorodimethyl-(9-fluorenyl)silane

Procedure:

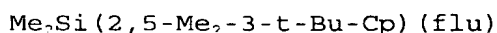
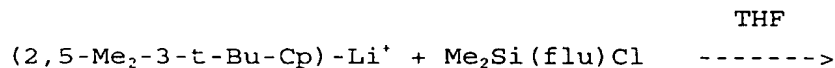
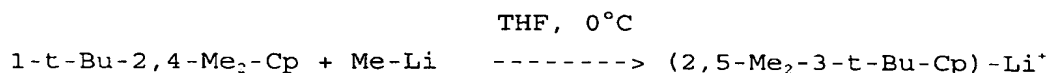
Into a 3000 ml flask, under nitrogen, was placed a solution of dichlorodimethyl silane (80.2 ml, 0.64 mol.) in 1000 ml of dry hexane, and the solution was pre-cooled to -78°C. A suspension

- 26 -

of fluorenyllithium (53.13 g, 0.32 mol.) in 2000 ml of hexane was slowly added via a cannula and the reaction mixture was stirred for an additional one hour at this temperature. The resulting mixture was gradually allowed to warm to room temperature and stirred for another 16 hours. The reaction mixture was then filtered under nitrogen, through a Celite plug (250 ml). The filtrate was concentrated and kept at -20°C overnight. The resulting light-green crystals were recrystallised from hexane at -20°C to afford 75.09 g (90.68 % yield) of chlorodimethyl-(9-fluorenyl)silane.

*E. Preparation of (2,5-dimethyl-3-*t*-butyl)-dimethyl-(9-fluorenyl)silane*

Reaction:



Procedure:

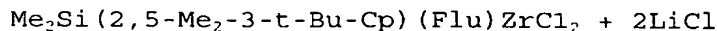
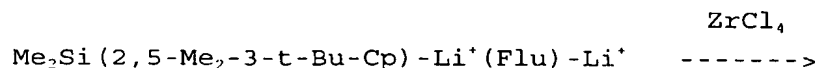
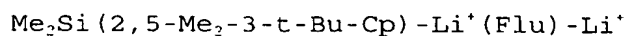
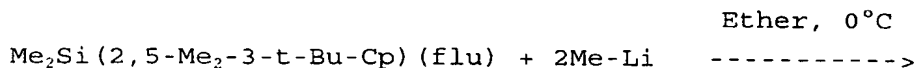
Into a 1000 ml flask, under nitrogen, was placed 10 g of 1-*t*-Bu-2,4-Me₂-Cp in 250 ml of dry tetrahydrofuran, and the solution was pre-cooled to 0°C. Then, a solution of 41.6 ml (0.0666 mol.) of methyllithium was added dropwise to the solution. After a stirring period, the reaction mixture was white. The reaction was further continued at room temperature for 4 hours. After that, a solution of 17.22 g (0.0666 mol.) of chlorodimethyl-(9-fluorenyl) silane in 80 ml of dry tetrahydrofuran was added dropwise to this solution. The reaction was further continued for 24 hours. The solvent of the organic phase was removed in

- 27 -

vacuo (10-2 mbar) at 40°C for 3 hours. The ligand was extracted with 2 x 300 ml of n-pentane. After filtration, the n-pentane was removed in vacuo at 40°C and yielded 23.75 g (95.72%) of a clear brown oil.

F. Preparation of dimethylsilyl(2,5-dimethyl-3-t-butyl-cyclopentadienyl)(fluorenyl)zirconium dichloride

Reaction:



Procedure:

In a 500 ml flask, under nitrogen, was placed 10 g of ligand in 100 ml of dry diethylether. The solution was pre-cooled to 0°C. A solution of 33.5 ml (0.0537 mol.) of methyllithium (1.6 molar/diethylether) was added dropwise to this solution. After a stirring period (24 hours), the solvent was removed in vacuo. The red powder was washed with 200 ml of pentane and yielded 12.4 g of a red power. Into a 500 ml flask, was placed the red dianion ligand, in 200 ml of pentane. 6.5 g (0.027 mol.) of zirconium tetrachloride was added to this suspension. The mixture was red-brown and the reaction was further continued for 24 hours in a glove box. After washing and filtration, the red powder was solubilised in 100 ml of dichloromethane. The solution was filtered and the filtrate was removed in vacuo and

- 28 -

yielded 13.2 g (92.3%) of orange powder.

Example 6: Polymerisation procedures II

Each polymerisation was performed in a 4 litre bench reactor with pure propylene or with diluent such as cyclohexane or isobutane with the quantities reported in the following Tables. Polymerisation was initiated by introducing metallocene (0.5 to 5 mg) precontacted with 1 ml of MAO (methylaluminoxane) (30% solution in toluene obtained from WITCO) three minutes prior to its introduction into the reactor.

Tables 7 and 8 show the results of polypropylene production using the catalyst of Example 5. Entries 1 to 4 compare polymerisation of pure polypropylene (bulk - entry 1) with those using the diluents cyclohexane (entry 2) and isobutane at two different partial pressures of hydrogen (entries 3 and 4). The polymerisation temperature for each of these entries was 60°C. It is apparent that a molecular weight of about 50,000 to about 150,000 was obtainable. Polypropylene having a melt temperature of at least 141°C was obtained. The polymers obtained exhibited monomodality on gel permeation chromatography (results not shown).

Table 8 shows the microtacticity of the polymer obtained using the catalyst according to Example 5 under polymerisation conditions as defined by the corresponding entries in Table 7. The results were obtained using ¹³C NMR spectroscopy. It will be apparent that the polypropylene contained more than 84% of pentads in the purely isotactic form (mmmm) and a virtually undetectable frequency of misinsertions.

Table 7: Bulk Polymerisation with 1-dimethylsilyl-(3-t-butyl 5-dimethylcyclopentadienyl-fluorenyl)
Zirconium dichloride

Entry	Pol Temp (°C)	Hourly Prod. (gPP/gCat/h)	MFI (g/10min)	Mn (KDa)	Mw (KDa)	Mz (KDa)	D	D'	Melt Temp (°C)
1	60	19.500	51.6	22.7	83.8	648.5	3.7	7.7	145.4
2	60	11.950	21.43	56.3	143.0	322.2	2.5	2.3	147.9
3	60	21.400	Too high	21.5	65.2	153.8	3.0	2.4	145.0
4	80	18.300	Too high	10.8	37.0	77.9	3.4	2.1	141.3

Key: MFI - Melt Flow Index, Mn=number average molecular weight, Mw=weight average molecular weight

D=Mw/Mn; D'=Mz/Mw

Table 8: Microtacticity with $\text{Me}_2\text{Si}(3\text{-tBu-2,5-dimethylene})\text{FluZrCl}_2$

Entry	Pol Temp	mmmm%	mmmr%	mmrr%	mrrm%	Inversion %	NMR Scans
1	60°C	89.3	3.6	3.4	1.6	0.11	4728
2	60°C	88.9	3.8	3.2	1.6	(1) or (2)	5840
3	60°C	86.1	4.8	3.9	1.9	(1) or (2)	1848
4	80°C	84.8	5.3	4.2	2.1	(1)	4236

(1): Inversions observed but too low to be quantified

(2): Not observed

- 31 -

CLAIMS:

1. A metallocene catalyst component for use in preparing isotactic polyolefins, which component has the general formula:



wherein C_p is a substituted cyclopentadienyl ring; C_p' is a substituted or unsubstituted fluorenyl ring; R'' is a structural bridge imparting stereorigidity to the component; R_1 is a substituent on the cyclopentadienyl ring which is distal to the bridge, which distal substituent comprises a bulky group of the formula XR^*_3 , in which X is chosen from Group IVA, and each R^* is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms, R_2 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and positioned *non-vicinal* to the distal substituent, and is of the formula $YR\#_3$, in which Y is chosen from group IVA, and each $R\#$ is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, R_3 is a substituent on the cyclopentadienyl ring which is proximal to the bridge and is a hydrogen atom or is of the formula $ZR\$_3$, in which Z is chosen from group IVA, and each $R\$$ is the same or different and chosen from hydrogen or hydrocarbyl of 1 to 7 carbon atoms, each R'_n is the same or different and is hydrocarbyl having 1 to 20 carbon atoms in which $0 \leq n \leq 8$; M is a Group IVB transition metal or vanadium; and each Q is hydrocarbyl having 1 to 20 carbon atoms or is a halogen.

2. A catalyst component according to claim 1, wherein R_1 is $C(CH_3)_3$, $C(CH_3)_2Ph$, CPh_3 or $Si(CH_3)_3$.

3. A catalyst component according to claim 2, wherein R_1 is $C(CH_3)_3$.

4. A catalyst component according to any one of claims 1 to 3, wherein Y is carbon.

- 32 -

5. A catalyst component according to any one of claims 1 to 4, wherein Z is carbon.
6. A catalyst component according to any preceding claim, wherein R_2 is CH_3 .
7. A catalyst component according to any preceding claim, wherein R_3 is CH_3 .
8. A catalyst component according to any one of the preceding claims, wherein R" is alkylidene having 1 to 20 carbon atoms, a dialkyl germanium or silicon or siloxane, alkyl phosphine or amine.
9. A catalyst component according to claim 8, wherein R" is isopropylidene or dimethylsilanediyl.
10. A catalyst component according to any one of the preceding claims, wherein M is zirconium or titanium.
11. A catalyst component according to any one of the preceding claims, wherein Q is halogen.
12. A catalyst component according to any one of the preceding claims, wherein the fluorenyl ring is unsubstituted at both positions 4 and 5.
13. A metallocene catalyst component for use in preparing isotactic polyolefins, which component comprises isopropylidene-(3-t-butyl-5-methyl-cyclopentadienyl fluorenyl) $ZrCl_2$, or dimethylsilanediyl-(3-t-butyl-2,5-dimethyl-cyclopentadienyl fluorenyl) $ZrCl_2$.
14. A metallocene catalyst component for use in preparing isotactic polyolefins, which comprises (i) a catalyst component according to any one of the preceding claims; and (ii) a regioisomer thereof in which R_2 is proximal to the bridge and

- 33 -

positioned *vicinal* to the distal substituent.

15. A metallocene catalyst component for use in preparing isotactic polyolefins, which comprises isopropylidene-(3-*t*-butyl-5-methyl-cyclopentadienyl fluorenyl)ZrCl₂ and isopropylidene-(3-*t*-butyl-2-methylcyclopentadienyl fluorenyl)ZrCl₂.

16. A catalyst system for use in preparing isotactic polyolefins, which comprises (a) a catalyst component according to any one of the preceding claims; and (b) an aluminium- or boron-containing co-catalyst capable of activating the catalyst component.

17. A catalyst system according to claim 16, which further comprises an inert support.

18. Use of a catalyst component according to any one of claims 1 to 13, and a co-catalyst which activates the catalyst component, for the preparation of isotactic polyolefins.

19. Use of a catalyst component according to claim 14 or claim 15, and a co-catalyst which activates the catalyst component, for the preparation of isotactic polyolefins having a multimodal molecular weight distribution.

20. A process for preparing isotactic polyolefins, which comprises contacting a catalyst system according to claim 16 or claim 17 with at least one olefin in a reaction zone under polymerisation conditions.

21. A process according to claim 20, wherein the olefin is propylene.

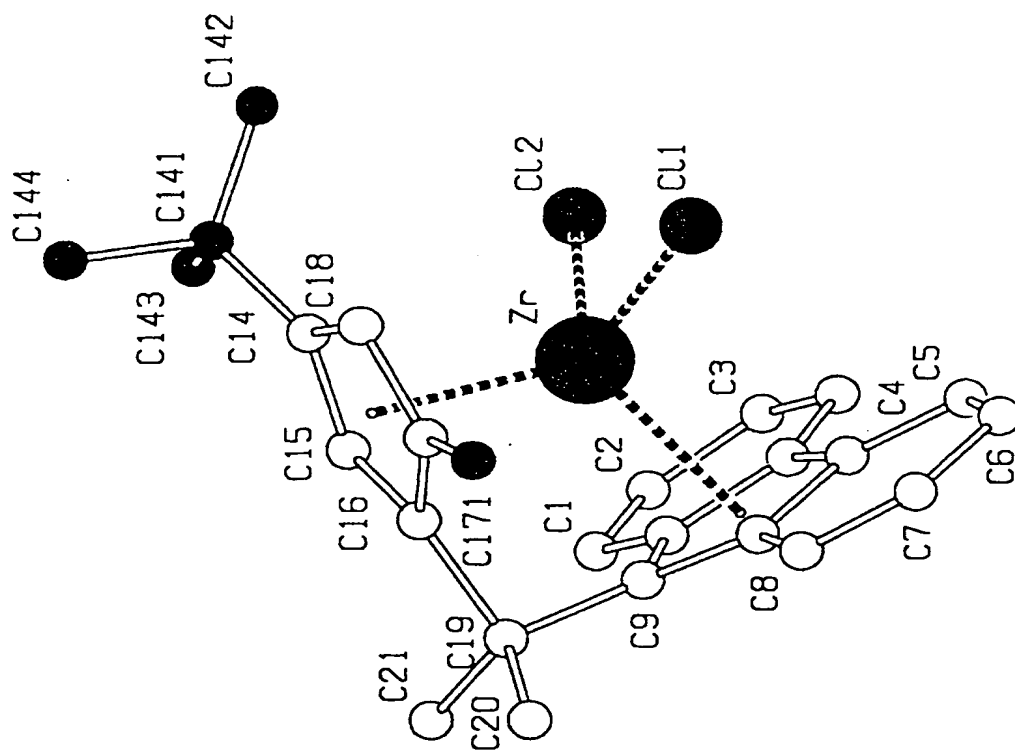
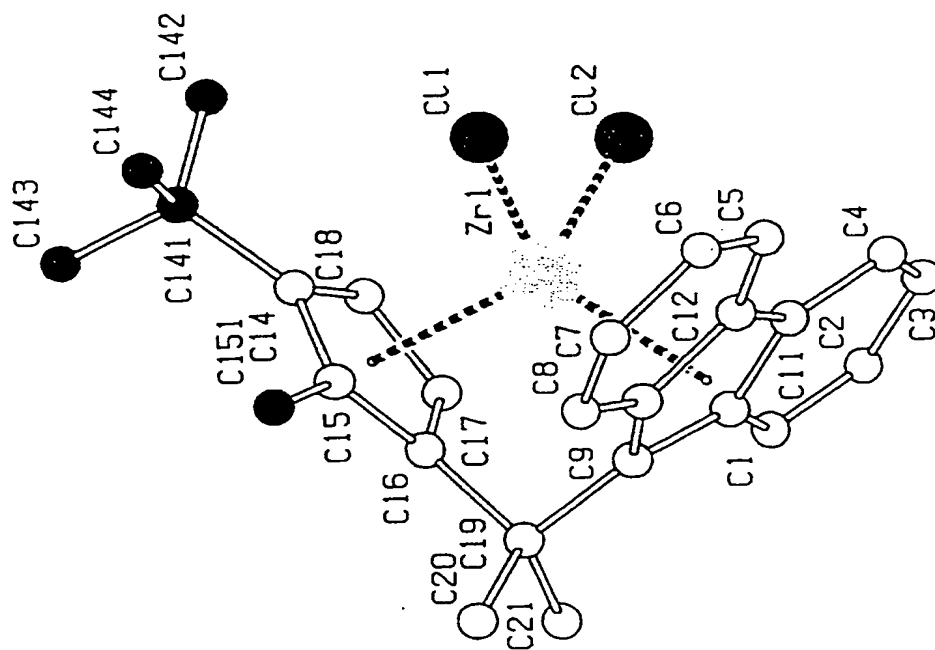


FIGURE 1



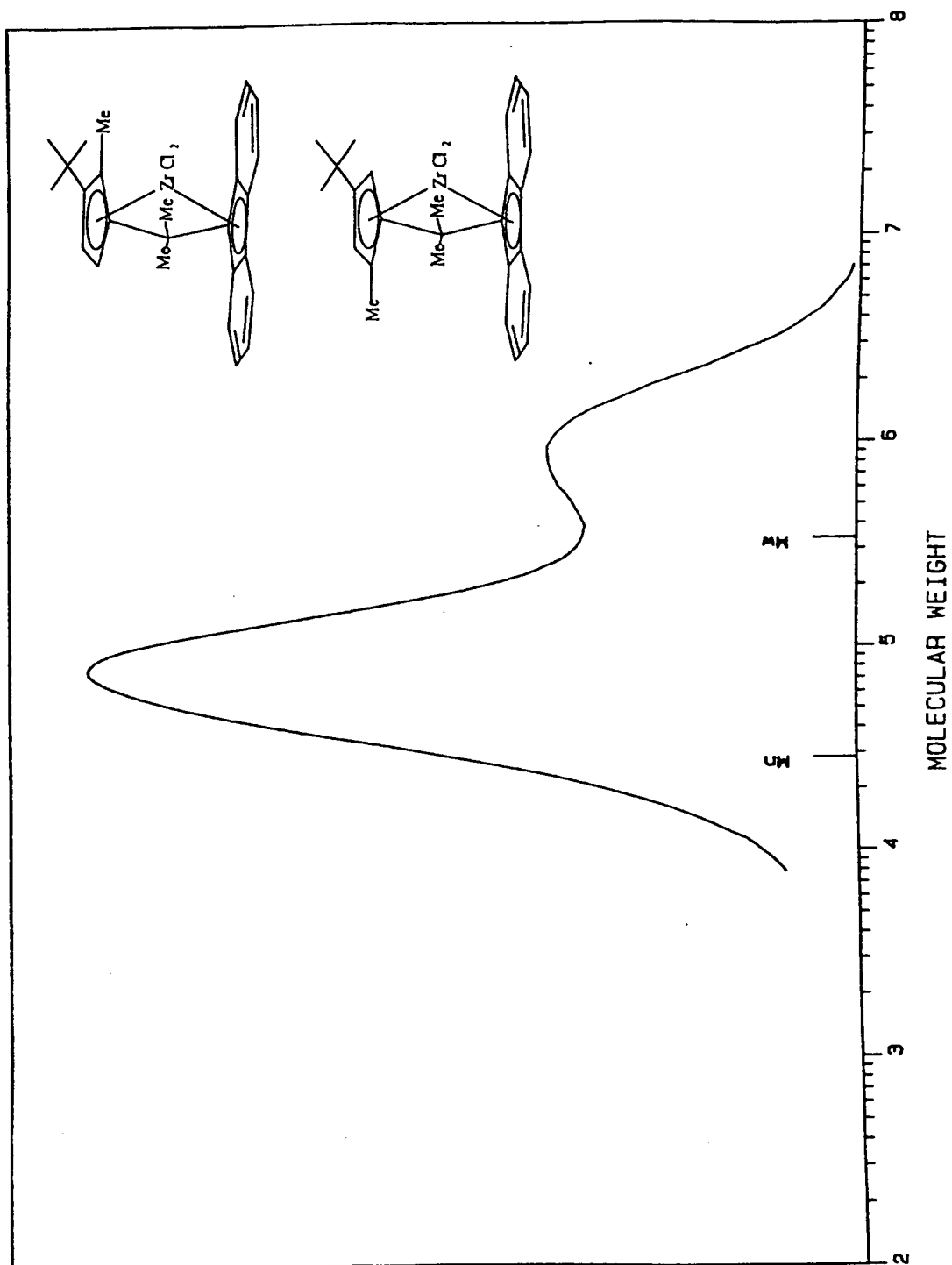


FIGURE 3

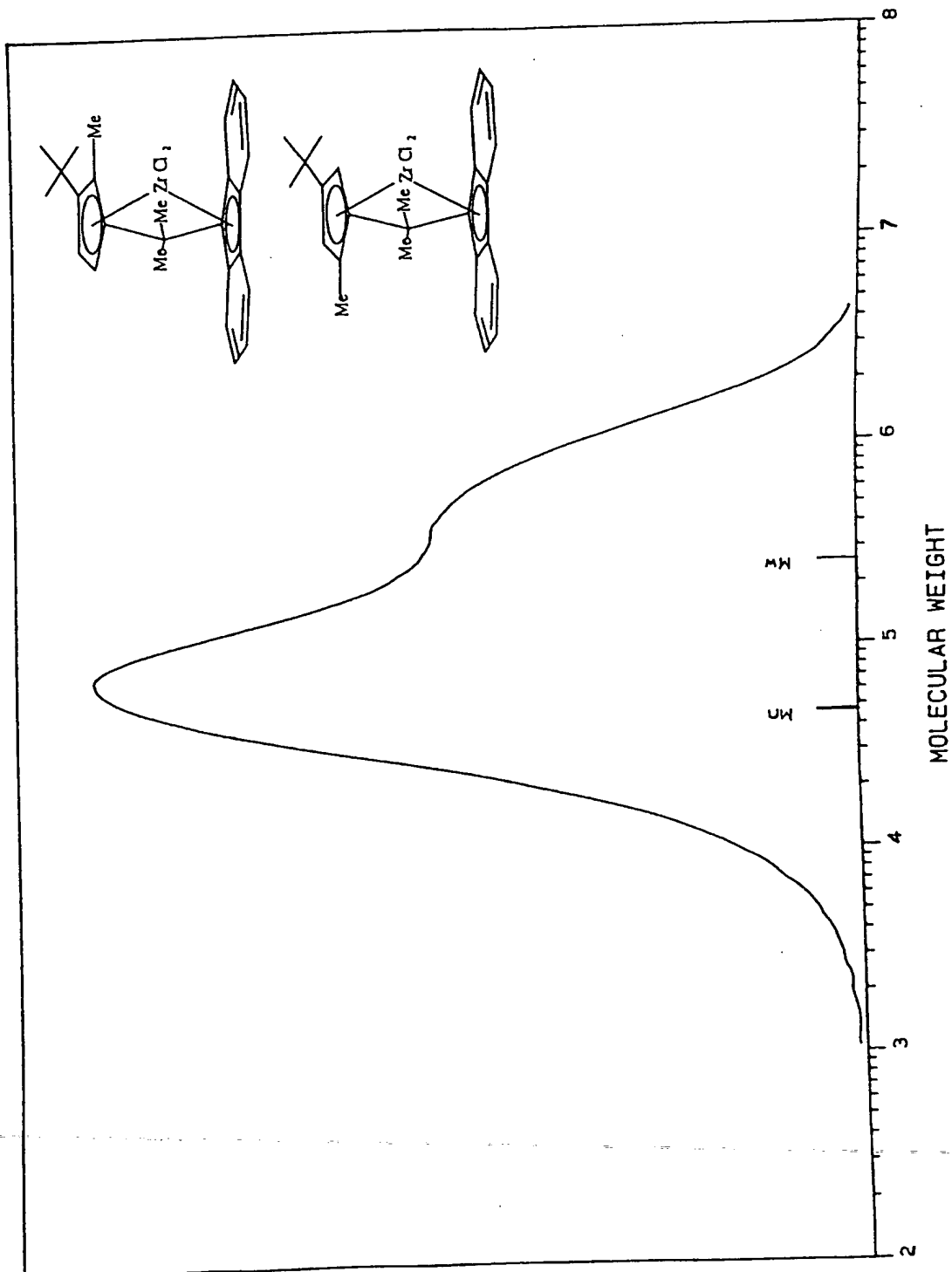


FIGURE 4

INTERNATIONAL SEARCH REPORT

Intern el Application No
PCT/EP 98/03099

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08F10/00 C08F4/642		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08F C07F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 631 202 A (EWEN JOHN A) 20 May 1997 see claims; col. 8, lines 45-48	1-21
A	US 5 459 117 A (EWEN JOHN A) 17 October 1995 see claims; col. 8, lines 21-27; col. 4, 29-30 and 42	1-21
A	EP 0 537 130 A (FINA TECHNOLOGY) 14 April 1993 cited in the application see claims	1-21
A	EP 0 747 406 A (FINA TECHNOLOGY) 11 December 1996 see claims	1-21
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 6 October 1998		Date of mailing of the international search report 16/10/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Mergoni, M

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/EP 98/03099

C.(Continuation) DOCUMENTS CONSIDERED T BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 693 497 A (DANUBIA PETROCHEM POLYMERE) 24 January 1996 see claims -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/03099

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5631202 A	20-05-1997	NONE	
US 5459117 A	17-10-1995	NONE	
EP 0537130 A	14-04-1993	US 5416228 A CA 2077713 A DE 69213878 D DE 69213878 T JP 6122718 A	16-05-1995 08-04-1993 24-10-1996 13-02-1997 06-05-1994
EP 0747406 A	11-12-1996	CA 2178411 A JP 9136930 A	08-12-1996 27-05-1997
EP 0693497 A	24-01-1996	AT 401519 B DE 4431643 A AT 145394 A	25-09-1996 07-03-1996 15-02-1996